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Thomas L. Beck, Michael E. Paulaitis and Lawrence R. Pratt
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Introduction

We consider a molecular description of solutions of one or more molecular components. An essential feature will be the complication of treating molecular species of practical interest since those chemical features are typically a dominating limitation of current work. Thus, liquids of atomic species only, and the conventional simple liquids, will only be relevant to the extent that they teach about molecular solutions. In this chapter, we will introduce examples of current theoretical, simulation, and experimental interest in order to give a feeling for the scope of the activity to be taken up.

The Potential Distribution Theorem (PDT) (Widom, 1963), sometimes called Widom's *particle insertion formula* (Valleau and Torrie, 1977), is emerging as a central organizing principle in the theory and realistic modeling of molecular solutions. This point is not broadly recognized, and there are a couple of reasons for that lack of recognition. One reason is that results have accumulated over several decades, and haven't been brought together in a unified presentation that makes that central position clear. Another reason is that the PDT has been primarily considered from the point of view of simulation rather than molecular theory. An initial view was that the PDT does not change simulation problems (Valleau and Torrie, 1977). In a later view, the PDT does assist simulations (Frenkel and Smit, 2002). More importantly though, it does give vital theoretical insight into molecular modeling tackled either with simulation or other computational tools, or for theory generally. This theorem has recently led to a new stage of molecular modeling of solutions, *quasi-chemical* theories that promise accurate molecular and chemical detail on the basis of available electronic structure computational methods of molecular science.

Our perspective is that the PDT should be recognized as directly analogous to the partition functions which express the Gibbsian ensemble formulation of statistical mechanics. From this perspective, the PDT is a formula for a thermodynamic potential in terms of a partition function. Merely the identification of a

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partition function does not *solve* statistical thermodynamics. But common ideas for approximate evaluation of partition functions can be carried over to the PDT. In contrast to Gibbsian partition functions, however, the PDT is built upon a local view of the thermodynamics and depends on local information. Therefore, the tricks from the common tool-kit work out simply and convincingly for liquids from the perspective of the PDT. In addition, the PDT gives a simpler perspective into some of the more esoteric ("... both difficult and strongly established ..." [Friedman and Dale, 1977]) results of statistical thermodynamics of molecular solutions. Thus, we present a point of view on the subject of molecular solutions that is simple, effective, and not developed elsewhere.

What follows is not a review. Nevertheless, there are old views underneath, and we do want to give the reader a valid sense of the scope, even historical scope, of the field.

Historical sketch

A genuine history is not offered here, but some historical perspective is required to appreciate what has been achieved. We suggest a natural division of that history into three periods: (a) a *pioneering* era prior to 1957 (the year that molecular simulation methods changed the field [Wood, 1986; Ciccotti *et al.*, 1987; Wood, 1996]), (b) the decade or so after 1957 when the theory of serious prototype liquid models achieved an impressive maturity, and (c) the present era including the past three decades, approximately.

Pioneering

The era before molecular simulation methods were invented and widely disseminated was a period of foundational scholarly activity. The work of that period serves as a basic source of concepts in the research of the present. Nevertheless, subsequent simulation work again revealed advantages of molecular resolution for developing detailed theories of these complex systems.

Students of this subject will remember being struck by the opinion expressed in the first English edition of the influential textbook *Statistical Physics* (Landau and Lifshitz, 1969), associated with this pioneering period:

> "We have not included in this book the various theories of ordinary liquids and of strong solutions, which to us appear neither convincing nor useful."

A sensitive evaluation of the truth content of this view – it would not be a general view (Kipnis *et al.*, 1996) – is less important than the historical fact that it should be flatly asserted in that setting.

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1957

The story of the initial steps in the development of molecular simulation methods for the study of liquids at the molecular scale has been charmingly recounted by Wood (1986; 1996). By 1957, these simulation techniques had been firmly established; the successful cross-checking of molecular dynamics calculations against Monte Carlo results was a crucial step in validating simulation methods for the broader scientific community.

Lots of ideas, many suboptimal, coexisted prior to the availability of the clear data that simulations provided. It was less that the simulations suggested new ideas than that the new simulation data served to alleviate the confusion of unclear ideas and to focus effort on the fruitful approaches. The theory of simple liquids treated by those simulations promptly made progress that we recognize, from our historical vantage point, as permanent. For example, the Percus–Yevick theory, proposed in 1957, was solved analytically for the hard-sphere case in 1963 (Wertheim, 1963; Thiele, 1963).

The PDT that is a central feature of this book dates from this period (Widom, 1963; Jackson and Klein, 1964), as does the related but separately developed scaled-particle theory (Reiss *et al.*, 1959).[1] Both the PDT and scaled-particle approaches have been somewhat bypassed as features of molecular theory, in contrast to their evident utility in simulation and engineering applications. Scaled-particle theories have been helpful in the development of sophisticated solution models (Ashbaugh and Pratt, 2004). Yet the scaled-particle results have been almost orthogonal to pedagogical presentations of the theory of liquids. This may be due to the specialization of the presentations of scaled-particle theory (Barrat and Hansen, 2003).

The theory of simple liquids wasn't simple

The theory of simple liquids achieved a mature state in the era 1965–1975 (Barker and Henderson, 1976; Hansen and McDonald, 1976). As this mature theory was extended towards molecular liquids, simple molecular cases such as liquid N_2 or liquid CCl_4 were treated first. But the molecular liquids that were brought within the perimeter of the successful theory were remote extremities compared with the liquids synthesized, poured from bottles or pipes, and used. In addition, the results traditionally sought from molecular theories (Rowlinson and Swinton, 1982) often appear to have shifted to accommodate the limitations of the available theories. Overlooking molecular simulation techniques

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[1] Kirkwood and Poirier (1954) had earlier used a result equivalent to the PDT in a specialized context, and Stell (1985) discusses Boltzmann's use of an equivalent approach for the hard-sphere gas.

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for the moment, it is difficult to avoid the conclusion that methods at the core of the theory of simple liquids stalled in treating molecular liquids of interest. A corollary of this argument is that molecular simulations overwhelmingly dominate theoretical activity in the theory of molecular liquids. The RISM (reference interaction site method) theory, then (Chandler and Andersen, 1972) and now (Hirata, 2003) an extension of successful theories of simple liquids, is an important exception. The luxuriant development of RISM theories highlights aspects of the theory of simple liquids that were left unsolved, particularly the lack of a "… theory of theories …" in the memorable words of Andersen (1975). Similarly, the introduction of the *central force models* for liquid water (Lemberg and Stillinger, 1975) broached the practical compromise of treating molecular liquids explicitly as complicated atomic liquids. A primary reason for those new models was that the theory of molecular liquids seemed stuck at places where the theory of atomic liquids was soundly developed. Despite the novelty of the central force models, the eventual definitive theoretical study (Thuraisingham and Friedman, 1983) of the central force model for water using the classic hypernetted chain approximation of the theory of simple liquids was disappointing, and highlighted again the lack of a theory of those theories of atomic liquids as they might be relevant to theories of molecular liquids.

The category of *simple* liquids is sometimes used to establish the complementary category of *complex* liquids (Barrat and Hansen, 2003). Another and a broad view of complex liquids is that they are colloid, polymer, and liquid crystalline solutions featuring a wide range of spatial length scales – sometimes called soft matter (de Gennes, 1992). Planting ourselves at an *atomic* spatial resolution, the models analyzed for those complex liquids are typically less detailed and less realistic on an atomic scale than models of atomic liquids.

In this book, simple liquids are contrasted with molecular liquids. Our goal is to treat molecular liquids on an atomic spatial scale. That doesn't mean approximations, perhaps even crude ones, won't sometimes be considered. But theories of molecular liquids, even with appropriate approximations, require molecule-specific features which the theory of simple liquids doesn't supply. As an example, the molecular liquid water is acknowledged here as a non-simple liquid, and a particularly complex molecular liquid.

1.1 Molecules in solution

Here we give a series of examples that illustrate our interest in molecules in solutions, and exemplify the problems that motivate the theory and modeling that is the subject of the remainder of this book. Many of the issues that are discussed physically here will be studied in detail in subsequent chapters.

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Reversed-phase liquid chromatography

Reversed-phase liquid chromatography (RPLC) is a workhorse technique for the separation of water-soluble chemical species. The method is used for chemical separations of molecular mixtures with sizes ranging from small molecules to biomolecules. Small differences in free energies, on the order of 0.1 kcal mol^{-1} for transfer between the aqueous mobile phase and the stationary phase of tethered alkanes, can lead to well-resolved chromatographic peaks following passage through the column. Understanding the driving forces for retention is thus a severe challenge to the theory of molecular liquids.

A typical RPLC column is packed with porous silica beads. The pore sizes have a length scale in the range 50–100 Å. The silica substrate is derivatized by a silanization reaction which attaches alkanes to hydroxyl groups on the surface. Chains of length 8–18 carbon atoms are utilized, with the C_{18} case being common. Surface densities up to about 50% of close packing are typical. The mobile phase most often contains a cosolvent, such as methanol or acetonitrile, in addition to water.

The flow rate is extremely slow on the time scale of molecular motions. Therefore, a quasi-equilibrium treatment is valid. The retention factor – the difference between the retention time for a peak of interest and a standard unretained reference, divided by the retention time for the reference – can then be taken as

$$k' = \Phi K, \tag{1.1}$$

where k' is the retention factor, Φ is the ratio of volumes of the stationary and mobile phases, and K is an equilibrium constant for solute partitioning between the two phases. The equilibrium constant is

$$K = \exp\left[-\beta \Delta \mu^{\mathrm{ex}}\right], \tag{1.2}$$

involving the excess chemical potential difference for the solute between the mobile and stationary phases. Thus, equilibrium statistical mechanics provides a framework to examine the free energy driving forces for retention.

Extensive experimental, theoretical, and modeling work has been directed at revealing details of the complex interface between the mobile and stationary phases (Beck and Klatte, 2000; Slusher and Mountain, 1999; Zhang *et al.*, 2005). Current debates are centered on the issue whether retention can be correctly understood as bulk liquid-phase partitioning or an adsorption process. The simulation work has shown that it is really neither of these two extremes; the interface possesses specific ordering features that present a non-bulk environment, yet nonpolar solutes do penetrate significantly into the

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stationary phase. Also, the measured excess chemical potential change is typically in line with bulk partitioning values.

Figure 1.1 shows a snapshot of the interface between a C_{18} stationary phase (at 50% coverage) and a 90/10, by volume, water/methanol mobile phase. Clearly the stationary phase is disordered, with little penetration of the aqueous phase into the stationary phase.

The density profiles for the 90/10 mobile-phase case of Fig. 1.1 are shown in Fig. 1.2. Notice the layering of the alkane chain segments near the solid surface. The chains topple over and pack into a disordered layer on the surface in order to fill the available volume. The chain segments never attain a flat density profile, so this region cannot be considered a bulk alkane fluid. In addition, the first 10 Å of the stationary phase near the silica support is glassy, while the tails exhibit liquid-like diffusive motion. The width of the stationary phase is about 18 Å, smaller than the fully extended length of 24 Å. The aqueous mobile phase does not penetrate significantly into the stationary phase, which is expected for aqueous/hydrophobic interfaces. Notice also the build-up of methanol at the interface, consistent with the observed reduction in surface tension in water/methanol mixtures. Previous simulations (Beck and Klatte, 2000) have shown that, beyond the segregation to the surface, methanol molecules in the interfacial region preferentially point their nonpolar ends toward the stationary phase. The waters are not orientationally ordered at the interface to an appreciable extent.

The excess chemical potential profile for methane gives a first indication of the driving force for retention (Fig. 1.3). This profile was computed using the PDT discussed in this book. A methane molecule experiences a 2.5 kcal mol^{-1} free energy drop on passing into the stationary phase, consistent with a bulk partitioning value; the drop on the right is at the liquid/vapor interface.

The free energy contributions to the transfer energy can be separated into repulsive and attractive components by examining the excess chemical potential profile for hard-sphere solutes (Fig. 1.4). For the pure aqueous mobile phase case in Fig. 1.4, there is a clear free energy minimum at the interface, indicating an increase in available volume because of the weak interpenetration of the hydrophobic and aqueous components. Thus the purely repulsive contribution to the free energy drives the solute into the interfacial region, while the attractive component leads to an additional drop entering the interface and further penetration into the stationary phase due to interactions with the tethered alkanes. With an increase of methanol content, the excess free volume for the hard-sphere solute disappears, suggesting better penetration of methanol into the stationary phase. A lesson from these simulation studies is that molecular-level realism is required to tackle these complicated interfacial problems.

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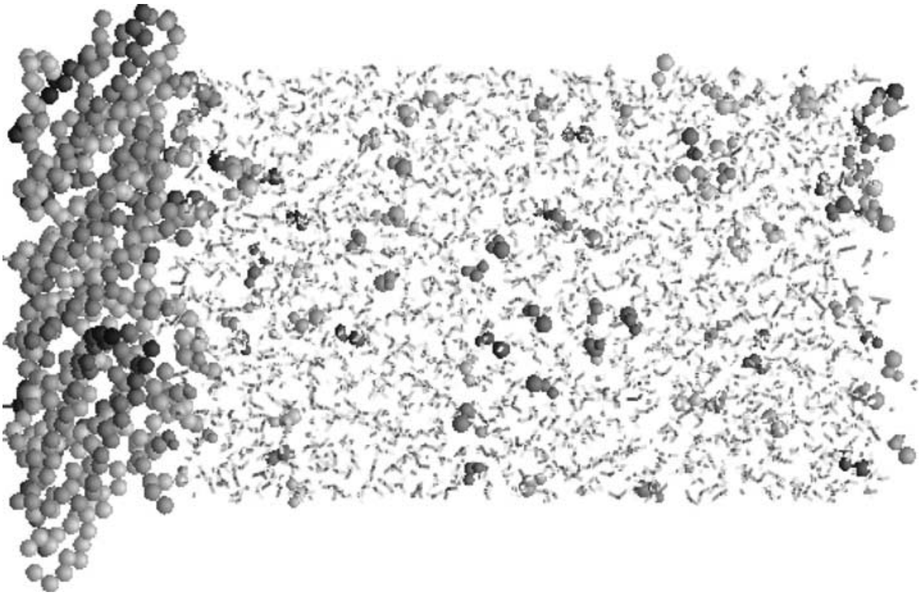

Figure 1.1 Snapshot of a reversed-phase liquid chromatographic interface. Tethered C_{18} chains are leftmost, displayed as ball-and-stick. The water/methanol mixture mobile phase, 10% methanol by volume, is on the right terminated by a fluid interface with vapor. Three-site model methanol molecules are also displayed as ball-and-stick, but the water molecules are wires only. (See Clohecy, 2005.)

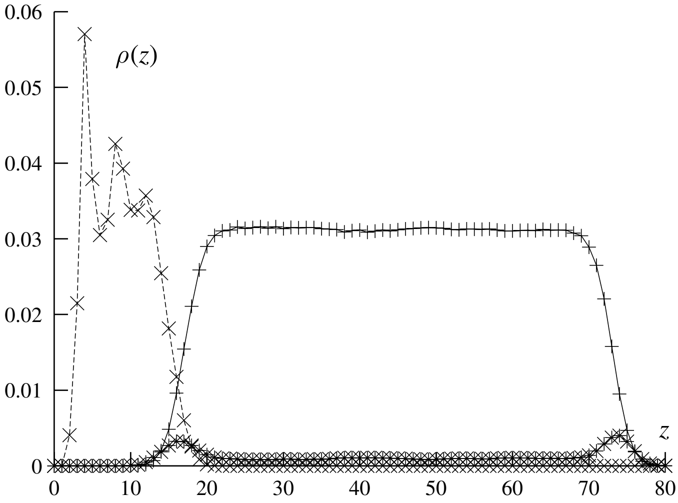

Figure 1.2 Number density profiles for the C_{18} carbon atoms, water oxygen atoms, and methanol carbon atoms for the 10% methanol case. The alkane carbon density is on the left, and the high-density profile is for water oxygen on the right. Distances along z perpendicular to the interfacial plane are given in Å. Densities are given in arbitrary units.

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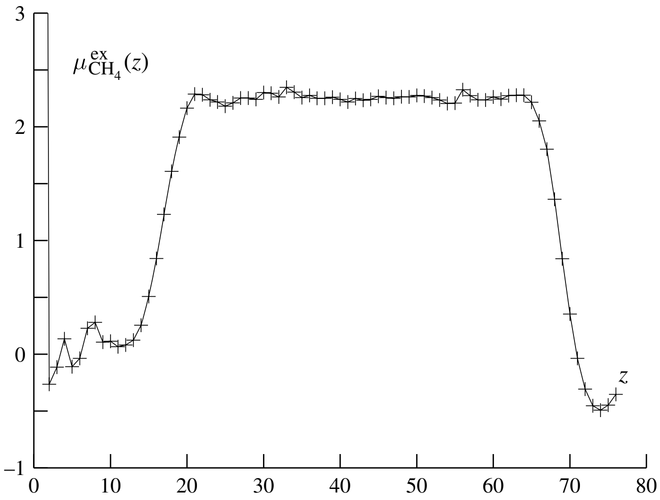

Figure 1.3 Excess chemical potential profile for methane for the 90/10 water/methanol mobile phase. Energies are given in kcal mol^{-1}. Distances along z perpendicular to the interfacial plane are given in Å.

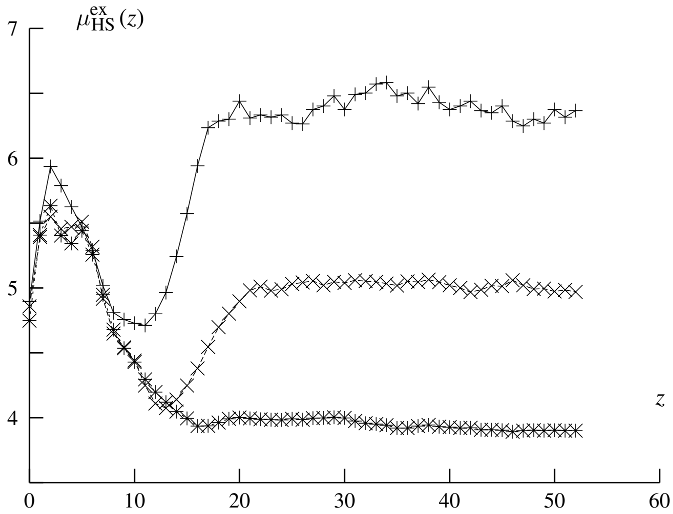

Figure 1.4 Excess chemical potential profiles (kcal mol^{-1}) for a 2.0 Å hard-sphere solute along the z axis. The C_{18} tethered chains are on the left. The three curves correspond to pure water (top), a 50/50 mixture (middle), and 90% methanol (bottom) by volume. Energies are in kcal mol^{-1}. Distances along z perpendicular to the interfacial plane are given in Å.

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Exercise

1.1 Compare expected free energy driving forces for retention of nonpolar *vs.* polar solutes in relation to the specific interfacial ordering effects in the RPLC system discussed above.

Variation of the dissociation constant of triflic acid with hydration

Nafion® is an archetypal proton-conducting material used in fuel-cell membranes. It is a Teflon®-based polymeric material with side chains ending with a hydrophilic sulfonic acid group. Because of these super-acidic head groups, Nafion® can be hydrated and can serve as a proton conductor separating electrochemical compartments. The consequences of variable hydration on proton conduction is expected to be significant for the performance of these materials. Experimental work has not yet fully resolved these issues, and a molecular understanding is still sought.

The important acid activity in Nafion® is appropriately represented by trifluoromethane sulfonic (triflic) acid, CF_3SO_3H; see Fig. 1.5. Dielectric spectroscopy has suggested that a significant amount of triflic acid is not dissociated in the ionic melt at 50% mole fraction of water (Barthel *et al.*, 1998). But the deprotonation chemistry of hydrated triflic acid hasn't been experimentally studied over the wide range of hydration and temperature that would be relevant to the function of sulfonate-based polyelectrolyte membrane materials.

Here we discuss a simple theoretical molecular model of triflic acid dissociation in dilute aqueous solution along the gas–liquid saturation curve to elevated

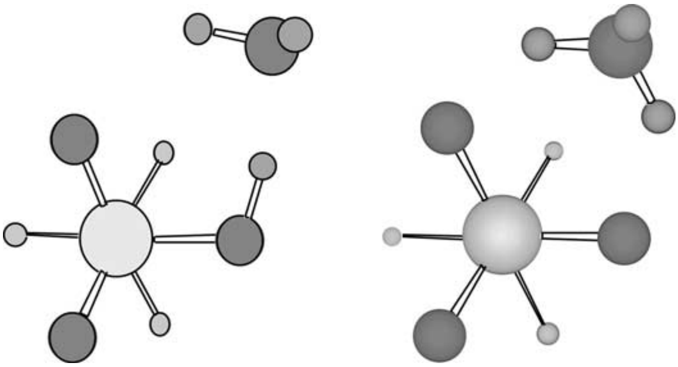

Figure 1.5 A trifluoromethane sulfonic (triflic) acid molecule, CF_3SO_3H, with one water molecule. The picture on the left shows the approximate minimum energy configuration of these molecules. The view is down the SC bond, with the SO_3 group closest to the viewer and the CF_3 behind. The picture on the right shows a configuration proposed as a transition state for scrambling of the acid hydrogen. (See Paddison *et al.*, 1998.)

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temperatures. The water liquid–vapor saturation curve serves as a simple reproducible path for reduction of the hydration of the triflic acid. These results are preparatory to molecular modeling at higher resolution (Eikerling *et al.*, 2003). Since data that would make this effort more conclusive are not yet available, these theoretical considerations might also serve to encourage further experimental work in this direction.

The approach here will be to take a specific triflic acid molecule, a *distinguished* molecule, as the basis for detailed molecular calculations, but to idealize the solution external to that molecule as a dielectric continuum. "External" will be defined as outside a molecular cavity established with spheres on each atom, characterized by radii treated as parameters. We will follow standard procedures in applying this dielectric model (Tawa and Pratt, 1994; 1995; Corcelli *et al.*, 1995). The specific goal below will be to treat the equilibrium

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{A}^- + \mathrm{H_3O}^+, \qquad (1.3)$$

with $\mathrm{A}^- = \mathrm{CF_3SO_3^-}$, over an extended range of conditions. The equilibrium ratio

$$K_\mathrm{a} = \frac{\rho_{\mathrm{A}^-}\rho_{\mathrm{H_3O}^+}}{\rho_{\mathrm{HA}}\rho_{\mathrm{H_2O}}} \qquad (1.4)$$

can be expressed as

$$K_\mathrm{a} = K_\mathrm{a}^{(0)} \exp\left[-\beta\Delta\mu^{\mathrm{ex}}\right], \qquad (1.5)$$

with

$$\Delta\mu^{\mathrm{ex}} \equiv \mu_{\mathrm{A}^-}{}^{\mathrm{ex}} + \mu_{\mathrm{H_3O}^+}{}^{\mathrm{ex}} - \mu_{\mathrm{HA}}{}^{\mathrm{ex}} - \mu_{\mathrm{H_2O}}{}^{\mathrm{ex}}, \qquad (1.6)$$

and μ_α^{ex} is the interaction contribution to the chemical potential of species α. The modeling of each μ_α^{ex} is the principal topic of this book. $\rho_\alpha = n_\alpha/\mathcal{V}$ is the number density or concentration of species α. The factor $K_\mathrm{a}^{(0)}$ is the equilibrium ratio found from the molecular computational results for the reactions without consideration of a solution medium; each of the interaction contributions of Eq. (1.6) may be estimated with the dielectric model. We will be interested here in conditions of infinite dilution of the solute but a wide range of conditions for the solvent; thus $\rho_{\mathrm{H_2O}}$ will vary widely. This warrants the appearance of the water density in Eq. (1.4), which is typically omitted when the water density has a standard value only.

Consideration of the isodesmic (Hehre *et al.*, 1970; McNaught and Wilkinson, 1997) Eq. (1.3) carries assumptions about the chemical state of the dissociated proton. Here our primary interest is the triflic acid, however, so we assume that this treatment is satisfactory for estimating hydration free energies without consideration of the involved issues of $\mathrm{H}^+(\mathrm{aq})$. If those assumptions were uncomfortable,